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INVESTIGATION OF THE IN SITU ACETYLATION PROCESS - DETERMINATION OF ENVIRONMENTALLY SIGNIFICANT CHLORINATED MONO AND DIHYDRIC PHENOLS IN AQUEOUS MATRICES USING DUAL CAPILLARY COLUMN GAS CHROMATOGRAPHY

R. Lega, O. Meresz and M. Savu, Ministry of the Environment, Laboratory Services Branch, Trace Organics Section, 125 Resources Road, Rexdale, Ontario, Canada M9W 5L1

Chlorophenols constitute a group of compounds with a long history of environmental problems. These problems started to occur at the turn of the century with the general introduction of chlorine-disinfection of public water supplies. The severe taste and odour problems were traced to chlorinated phenols and to phenols in the raw water, thus analysis of "phenolics" in the source waters is probably the earliest example of environmental monitoring for organic compounds at the trace levels. Later, wood pulp bleaching produced and introduced a wide variety of chlorinated phenolic compounds directly to the aquatic environment. These substances have very high pollution potentials owing to their fish toxicity, bioaccumulation and fish tainting properties. Other sources of chlorophenols are penta chlorophenol-based wood preservatives and pesticides synthesized from chlorinated phenols.

The objective of the present work was to develop a gas chromatographic analytical scan for a wide range of chlorophenolic compounds that can occur in the environment, including derivatives of dihydic phenols such as catechol and its monomethyl ether guaiacol.

Since phenolic compounds, in general, are notorious for causing difficulties in gas chromatography, a derivatization step had to be considered. For this purpose, in situ acetylation was selected as the technique of choice. This reaction is receiving increasing attention in organic trace analysis, as it is an elegant and simple technique that in one step achieves derivatization for gas chromatographic analysis and greatly improves recoveries of phenolic compounds from aqueous matrices.

A systematic study of the in-situ acetylation reaction was undertaken using selected phenols, and later the full range of analytes proposed for the scan. The full range of phenolic compounds is shown in Table 1.

TABLE 1. LIST OF CHLORINATED PHENOLIC COMPOUNDS INVESTIGATED

Chlorophenols

- | | |
|----------------------------|-------------------------------|
| 1. Phenol | 12. 2,4,6-Trichlorophenol |
| 2. 2-Chlorophenol | 13. 2,3,6-Trichlorophenol |
| 3. 3-Chlorophenol | 14. 2,3,5-Trichlorophenol |
| 4. 4-Chlorophenol | 15. 2,4,5-Trichlorophenol |
| 5. 2-Chloro-5-Methylphenol | 16. 2,3,4-Trichlorophenol |
| 6. 2,6-Dichlorophenol | 17. 3,4,5-Trichlorophenol |
| 7. 4-Chloro-3-Methylphenol | 18. 2,3,5,6-Tetrachlorophenol |
| 8. 3,5-Dichlorophenol | 19. 2,3,4,6-Tetrachlorophenol |
| 9. 2,3-Dichlorophenol | 20. 2,3,4,5-Tetrachlorophenol |
| 10. 2,4-Dichlorophenol | 21. Pentachlorophenol |
| 11. 3,4-Dichlorophenol | |

Chloroguaiacols

- | | |
|-----------------------------|---------------------------------|
| 22. 4-Chloroguaiacol | 25. 4,5,6-Trichloroguaiacol |
| 23. 4,5-Dichloroguaiacol | 26. 3,4,5,6-Tetrachloroguaiacol |
| 24. 3,4,5-Trichloroguaiacol | |

Chlorocatechols

- | | |
|--------------------------|-----------------------------|
| 27. 4-Chlorocatechol | 29. 3,4,5-Trichlorocatechol |
| 28. 4,5-Dichlorocatechol | 30. Tetrachlorocatechol |

Others (non Primary Target)

- | | |
|-----------------------------|--------------------|
| 31. 3,4,5-Trichlorosyringol | 33. Guaiacol |
| 32. 5,6-Dichlorovanillin | 34. Syringaldehyde |

During the study, the following variations were explored:

1. Running the acetylation without and with bicarbonate buffer.
2. Addition of extraction solvent before or after the main acetylation reaction.
3. Addition of 2.5 or 5.0 mL acetic anhydride to 500 mL sample.
4. Addition of acetic anhydride in one or two portions.
5. Absence or presence of a catalyst.
6. Addition of different catalysts:
 - a) 4-(dimethylamino)pyridine
 - b) pyridine
 - c) eucalyptol
7. Single/multiple extraction.
8. Direct/stepwise evaporation of extract.

The following observations were made:

1. In the absence of bicarbonate buffer, acetylation does not take place to a practically acceptable extent.
2. The addition of extraction solvent (methylene chloride) after 15 min. reaction time (and not before the addition of acetic anhydride) resulted in little changes in recoveries with the exception of guaiacols. The recovery of tetrachloroguaiacol doubled, from 41 to 82% (average of eight experiments).
3. Doubling the quantity of acetic anhydride (from 2.5 to 5.0 mL) had little effect on recoveries.
4. The addition of acetic anhydride (5.0 mL) in two 2.5 mL portions made little difference in recoveries.
5. Addition of catalyst generally increases recoveries especially for those components which are difficult to acetylate (such as guaiacols, syringaldehyde).
6. Pyridine and 4-(dimethylamino) pyridine showed comparable catalytic effects while eucalyptol had a very slight positive effect on the reaction.
7. Multiple extraction of the reaction mixture gives slightly higher recoveries when the same total quantity of solvent is used but the difference does not justify the effort required.
8. Stepwise evaporation of dried extracts gave slightly lower but more consistent recoveries.

Sample extracts were analysed on a Hewlett Packard 5730A Gas Chromatograph equipped with dual flame ionization detector and dual capillary column (30m, 0.25mm ID, 0.25µ coating DB17 and DB1).

The method detection levels of all the compounds were calculated according to the Ontario Ministry of the Environment guidelines, and were found to be in the range 2-5 µg/L.



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